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Microbial transformations of uranium and environmental restoration through bioremediation

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ABSTRACT: Microorganisms present in the natural environment play a significant role in the mobilization and immobilization of uranium. Fundamental understanding of the mechanisms of microbiological transformations of various chemical forms of uranium present in wastes and contaminated soils and water has led to the development of novel bioremediaition processes. One process uses anaerobic bacteria to stabilize the radionuclides and toxic metals from the waste, with a concurrent reduction in volume due to the dissolution and removal of nontoxic elements from the waste matrix. In an another process, uranium and other toxic metals are removed from contaminated soils and wastes by extracting with the chelating agent citric acid. Uranium is recovered from the citric acid extract after biodegradation/photodegradation in a concentrated form as $UO_3 \cdot 2H_2O$ for recycling or appropriate disposal.

1 INTRODUCTION

Microorganisms are known to immobilize uranium by (i) bioaccumulation and biosorption by microbial biomass and biopolymers; and (ii) reductive precipitation from higher to lower oxidation state by enzymatic action. These processes have received considerable attention because of their potential application in the remediation of uranium contaminated soils, aqueous waste streams, and wastes (Francis, 1999).

1.1 Bioaccumulation and Biosorption

The ability of microorganisms and the polymers secreted by them to scavenge metal ions has been extensively studied. Microorganisms, whether living or dead, possess an abundance of functional groups such as carboxylate, hydroxyl, and phosphate on their cell surface that bind uranium. Although intracellular accumulation of uranium has been reported, the mechanism of transport which usually occurs by an energy-dependent transport system, has not been elucidated. Polymers secreted by many actively metabolizing microbes also immobilize metals.

1.2 Immobilization due to reductive processes

Reduction of an element from a higher to a lower oxidation state or to elemental form affects its solubility resulting in the precipitation of several metals. For example, a variety of microorganisms convert hexavalent uranium to the tetravalent state by enzymatic action. The direct implication of microorganisms in the reduction of uranium is of considerable interest because of its potential application in bioremediating contaminated sites by immobilizing the uranium *in situ*.

$$U(VI)_{aq} \xrightarrow[\text{fermenters, sulfate reducres}]{\text{dissimilatory metal reducers}} U(IV)_S$$

The reduction of uranium was reported in axenic cultures of iron-reducing bacteria, fermentative bacteria, sulfate-reducing bacteria, and cell-free extracts of *Micrococcus lactilyticus*, and in uranium wastes by *Clostridium sp* (Figure1). Reactive barrier technology is based on the activities of these anaerobic bacteria. However, the long-term stability of the immobilized uranium is not known.

2 URANIUM STABILIZATION BY REDUCTIVE PRECIPITATION

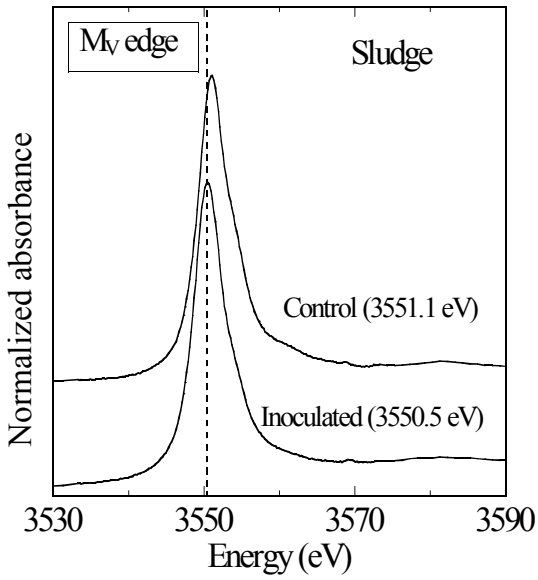

Figure 1. X-ray absorption near edge spectra (XANES) of sludge treated with anaerobic bacteria showing reduction of U(VI) to U(IV).

Treatment of uranium- and toxic-metal contaminated sediment and sludge with the anaerobic bacterium *Clostridium sp*. removed a large fraction of soluble non-toxic metals such as Ca, K, Mg, Mn^{2+}, Na, and Fe^{2+}, enriched and stabilized Cd, Cr, Cu, Ni, Pb, U and Zn, and

reduced the overall volume and mass. In this novel approach to treating wastes, the unique metabolic capabilities of the dual-action anaerobic bacteria were exploited to solubilize and/or precipitate radionuclides and toxic metals directly by enzymatic action and indirectly by the production of organic acid metabolites. The non-hazardous materials in the solid phase were solubilized and removed from the waste, thereby reducing its volume. The remobilized radionuclides and toxic metals are stabilized by precipitation reactions and redistributed with stable mineral phases of the waste (Francis et al., 1991, U.S. Patent 5,047,152).

3 REMOVAL AND RECOVERY OF URANIUM FROM CONTAMINATED SOILS AND WASTES

For decontamination, uranium must be removed and recovered from the contaminated site, so that the site is restored. Various soil washing techniques have been developed including physical methods, such as wet-screening, attrition scrubbing, or chemical methods consisting of treating with organic and inorganic acids, salts, bases, and chelating agents. For example, nitric acid, hydrochloric acid, phosphoric acid, sulfuric acid, sodium carbonate, ammonium carbonate, sodium hydroxide, oxalic acid, citric acid, EDTA, and DTPA have been used to extract radionuclide and toxic metals. Many of the inorganic chemicals used are corrosive, which irreparably damages the soil. Furthermore, all chemical extraction methods generate secondary waste streams which create further problems of hazardous waste disposal.

Among the several organic complexing agents used in extracting metals, citric acid appears to be the most preferred because it is a naturally occurring organic complexing agent. It is environmentally friendly, exhibits relatively consistent removal efficiency, and is cost-effective. Citric acid extract is subjected to biodegradation, followed by photodegradation. Several metal citrate complexes are readily biodegraded, and the metals are recovered in a concentrated form, along with the bacterial biomass. Uranium forms a binuclear complex with citric acid and is recalcitrant. The supernatant containing this complex is separated, and exposed to light; it rapidly degrades with the precipitation of uranium. Uranium is recovered as $UO_3 \cdot 2H_2O$ in a concentrated form for recycling, or for disposal (Figure 2). This treatment process, unlike others, does not generate additional hazardous wastes for disposal and causes little damage to the soil which is then be returned to normal use (Francis and Dodge, 1998).

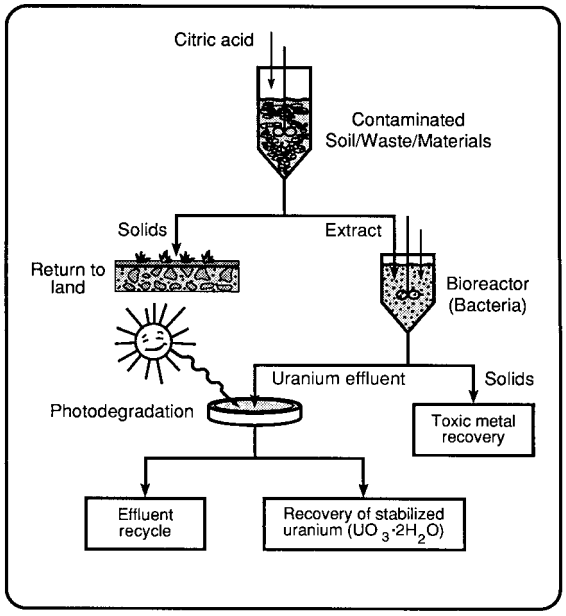

Figure 2. Citric acid treatment process (Francis and Dodge, 1994, U.S. Patent No. 5292456)

This process has significant potential for commercialization because (i) it can be applied to a variety of materials and waste forms; (ii) mixed waste is separated into radioactive and hazardous waste; (iii) uranium is separated from the toxic metals and recovered for recycling or disposal; (iv) it does not generate secondary waste streams; (v) it causes little damage to soil; and (vi) environmentally and economically important metals are removed in a concentrated form. The use of combined chemical, photochemical, and microbiological treatments of contaminated materials will be more efficient than present methods and result in considerable savings in clean-up and disposal costs.

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